

Introduction to Chemical Thermodynamics and Kinetics
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Lecture – 32
Chemical Kinetics: Mechanisms – Part 1

Now, that rate law actually that rate equation is often proportional to the some power of the reactants. It can be also a proportional to some integral power or fractional power of the products also and then we can define the order of the reaction.

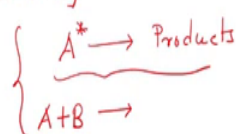
However, if we cannot write it in terms of a simple equation like where the overall rate equation of the rate is proportional to the product of concentration terms. And each term is raised to some integral or fractional power then the order does not have any meaning.

And today we will see that we give an example that how the reaction between very simple reaction between hydrogen and bromine which apparently seems to be bimolecular reaction, but actually it is a very complicated reaction; it is a overall composite reaction which is composed of many many elementary reactions and then we see a very complicated expression for the rate.

But not only the reactants come into the rate law concentration of the reactants but also the products coming to the rate law. So, today we will discuss that mechanism as well as my few other reactions mechanism of few other reactions. And we will see how to device a mechanism successfully so, that it satisfied the overall rate law which is experimentally observed. Now, to begin with let us first define what is an elementary reaction?

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Elementary reactions:



$$\text{Rate} = k[A] \quad \text{unimolecular}$$

$$= k[A][B] \quad \text{bimolecular}$$

$$= k[A][B][C]$$



So, by the name as the name suggests you can ask this question why all of a sudden a molecule is forming a product. It must be some energized molecule meaning that we had a molecule and that due to thermal heating which means heating means always collision with other molecules or some by some other activation.

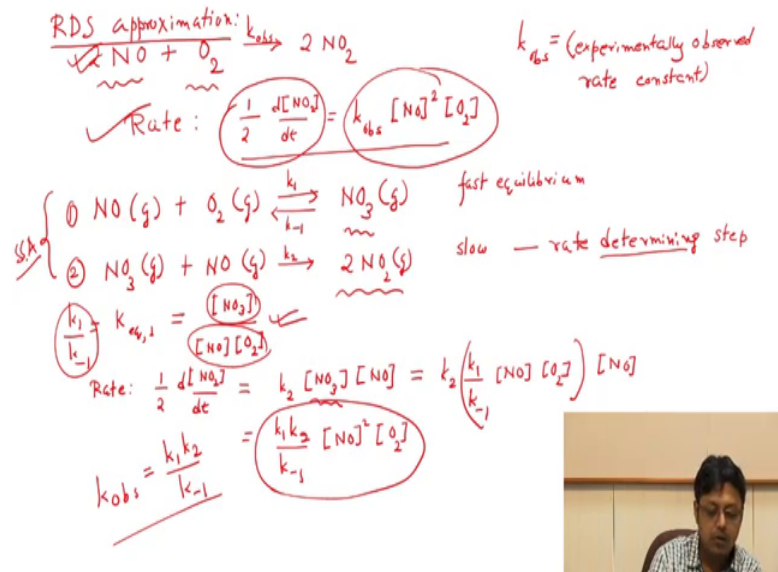
Say for example, by shining light on it, it can actually go to some higher excited state and then we call it as an energized molecule. And that energized molecule can give rise to product and then the rate for elementary reactions, we can always write it as the reaction is written I mean in the stoichiometry or the balanced equation.

So, we can write it like $k[A]$ because this is a fundamental step and for a biomolecular reaction if it is something like more general type $A + B$ going into product. So, the rate will be equal to $k[A][B]$; now elementary reactions are always unimolecular or bimolecular because the probability of having more than two molecules collide simultaneously and giving a product will be very very low. Usually in the gas phase or liquid phase the collisions which we observe are dominated by bio molecular collisions.

So, these kind of reaction if we find that we have three species and giving rise to some product then we cannot say that it is a limit again; we cannot also write it as $A \rightarrow B \rightarrow C$ ah; this is this is actually wrong because it must be then a composite reaction which is can be broken into elementary bimolecular as well as human molecular reactions.

Now, so, elementary reactions are always classified as unimolecular and bimolecular reactions. Now we will discuss both of these together, but first we will start with the bimolecular reaction. So, we have two components A and B and giving rise to some product and for unimolecular reactions we have a model we have a kinetic model that also we will discuss today.

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Now, the first thing is let us take an example and like the nitrogen dioxide example we; started discuss the formation of nitrogen dioxide from nitric oxide and oxygen. And this actually form nitrogen dioxide with some rate constant and that rate constant I am writing at k suffix obs; obs means actually it is a observed a rate constant. So, ke obs is observed or better to write it as a experimentally observed rate constant experimentally observed rate constant.

Now, the question is how the rate law for this reaction will look like. The rate law we found that also was experimentally determined which we can write it as formation of in terms of nitrogen dioxide formation dno to dt or we can also could we could also write it in terms of the concentration of nitric oxide or oxygen with a negative sign. And each time we write it to the coefficient or the stoichiometric coefficient will come in the denominator. And the negative sign will come for the reactants well positive sign will be considered for the products.

Now, that we found that it follows our rate law like this and as you said that three body collisions are rare. So, this is not an elementary reaction where 2 nitrogen nitric oxide molecules and 1 oxygen molecule collated simultaneously at the same time to produce the product which is nitrogen dioxide. It must be broken into smaller steps which are which now we are going to discuss.

Now, the first mechanism we are going to by the way the mechanisms can be of one particular reaction, can have very different mechanism. And each mechanism of course, by mechanism we mean that the each mechanism or each model actually satisfactorily explains these observed rate law. Because this is what we are getting experimentally and we have to explain or we have to get at the end of the day and expression fraud which actually matches the experimental observed rate law.

Now, let us consider an model; so, that first model says that the first step nitric oxide gas and oxygen gas reacts in a bimolecular reaction and that is in forms nitrogen dioxide. Now if you see the equation the stoichiometric equation NO_2 does not come into picture; So, NO_3 must be an reaction intermediate which you do not observe. And in the second step these nitrogen trioxide gas reacts further with nitric oxide to form 2 molecules of nitrogen dioxide they are all gas phase species.

So, we divided the entire reaction which is a composite reaction; which is expressed by these stoichiometric I mean this reaction which has perfect chemical stoichiometric. But we are saying now this reaction can be broken into two elementary reactions; each of them is bimolecular elementary reaction. And in the first case first reaction we considered a very fast equilibrium between the reactants and products; it is a reversible reaction the first one and the second one is actually slow reaction.

Now, if you have many elementary reactions happening together; the overall rate will of course, be dependent on the slowest reaction. And we can have an analogy for example, suppose you have you have many lens and where cars are going on road and then there is a bottleneck. And then we can easily judge that the overall speed of the cars or the average speed will be actually dominated by the speed of the slowest moving cars because they are creating the bottleneck in the in the road.

So, these low similarly in the similar way these slow if it is a slow reaction or the slowest step type of in a composite reaction; so, that reaction will control the overall rate. So, the

overall rate will be determined by the slowest rate step or the that particular elementary reaction that has the that occurs at a slowest speed. So, that step we call it as rate determining step because it determines the overall rate it is a determining step.

Now, let us consider how we devise a mechanism, also consider that we have some rate constant for these forward reaction of the first process and as well as the reverse reaction, And the second reaction rate constant I am writing as k_2 ; so, considering the first equilibrium, we can always write that there is some equilibrium constant I am just writing k equilibrium suffix 1 to denote that it is a first reaction; first elementary step and for that we can write it as this is nothing, but NO_3 divided by NO divided by O_2 .

So, this is from the first reaction; now the overall rate of the reaction as we said will be controlled by their rate determining step and you can see actually the NO_2 is formed in this step; So, the formation of NO_2 if you just considered the second reaction. So, the rate will be given by rate of the second reaction which is $d\text{NO}_2/dt$ which is actually the rate of the overall reaction.

So, you can see the overall reaction rate is controlled by the slowest step is according to the second equation is $k_2 \text{NO}_3 \text{NO}$, but we know that NO_3 can now be replaced by this. And this equilibrium constant remember is nothing, but the ratio of the forward rate constant divided by reverse rate constant for step 1.

So, you can write now right away actually replace the NO_3 concentration by this particular expression which we just got. So, it will be k_2 instead of NO_3 we are writing it as k_1 by k_{-1} multiplied by NO into O_2 . So, that is for NO_3 and it was then multiplied by NO . So, you can easily rearrange it you can see that it will be nothing, but k_1 by $k_{-1} k_2$ by k_{-1} into NO^2 into oxygen.

So, you can see the rate law now satisfactorily describes the observed rate law; where we discovered that this k_{observed} is nothing, but a combination of rate constants of elementary step and this is the expression for k_{observed} . So, this is a mechanism which satisfactorily explained our observed rate law which is actually some rate constant times the nitric oxide concentration squared, times the oxygen concentration and we found we can satisfactorily explain.

However we still do not know whether this mechanism is correct or not; you can actually come up with something and some model and which satisfactorily explains it. Now remember that here the assumption is that the NO_3 actually is formed as an intermediate nitrogen dioxide. So, in order to demonstrate that your model is correct or not; you have to show that this nitrogen dioxide NO_3 is a species that was generated.

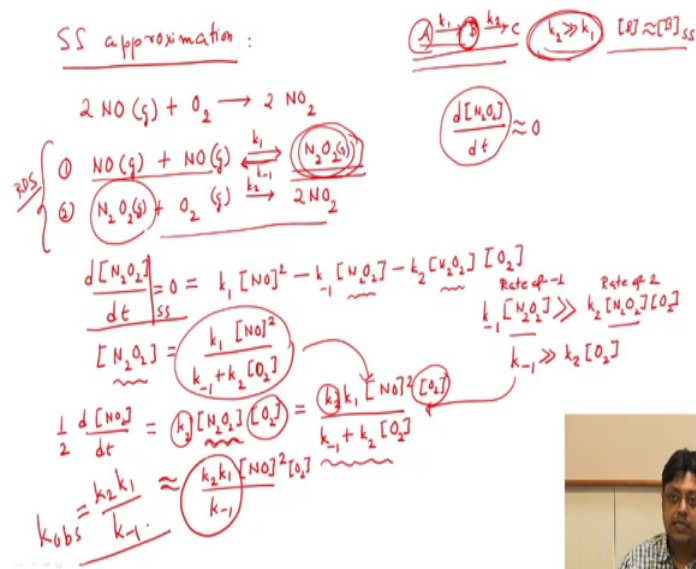
Now, you can actually do some experiments which are called reactive intermediate cracking experiments. Because usually this intermediates will be very shortly; they are formed and then and there they react because they will be very reactive to form the product.

So, this intermediate sometimes you can actually go to very low temperature freeze the collision momentarily and then or trap it in a matrix. And then you can actually do some spectroscopy which actually will tell you whether this species NO_3 is present in your mixer or not. If you can identify yes NO_3 is present in this mixer; then actually it supports this mechanism. I will show that there is another mechanism that we can propose for this reaction that also satisfactorily describes this reaction.

Now, point number 2 here is that we learnt one interesting thing and composite reaction can be broken into elementary steps. and this is one way of breaking a composite reaction into elementary step where we considered first equilibrium in the first step and then there is a slow rate determining step. So, overall this kind of mechanism is known as a rate determining step or RDS approximation. So, we just what we can just did is proposing a mechanism based on this RDS approximation or rate determining step approximation.

We will now consider the other approximation; so, this is nothing, but RDS approximation or the rate determining step approximation, where we approximated the or constructed a model based on the approximation that there is a slow step which is the rate determining for the overall reaction. Now, similarly we can propose an another mechanism which is known as steady state approximation.

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Now, already we discussed in the previous lecture what is the steady state concentration of the intermediate? If you remember that we considered a consecutive reaction of the type A is going to B and going to C with some rate constant k_1 and k_2 . And we showed that under the condition k_2 much much greater than k_1 ; the concentration of B reaches steady state concentration which is basically remains constant over time after some period which is known as the induction period.

Now, we will consider a slightly different version of this; in the sense that we are explaining the same reaction to NO gas plus oxygen giving rise to 2 NO₂. And then we will consider the steps in a slightly different manner; we will say that first there is nitrogen gas and first the true nitric oxide gas react together to form N₂O₂; now you see that there is a different species here.

So, that is step 1 and then this N₂O₂ reacts with oxygen to form 2 molecules of nitrogen dioxide. Now stoichiometrically this is fine if I just add 1 and 2 that is also giving rise to the same thing, but here I am not considering an equilibrium step in the first case. And whatever we are trying to say here is that we have rate and then we have to have basically two reactions. So, let us first compare with this equation.

So, if you write it in this way; now you can see that I have a similar situation where I have to approximate that this concentration of this intermediate which is N₂O₂ is actually has reached the steady state concentration after some time. Which means I will

approximate this change; steady state means the concentration is almost constant will be almost equal to 0. So, we have to just find first a rate law for the intermediate concentration and then put it 0 and then we are done.

However, in this model we will slightly modify it little bit. So, we will say that actually there was a equilibrium because just we are keeping an analogy with the earlier case; where we said that there is a fast equilibrium exists and there is a slow rate determining step. Here we are considering slightly different thing; we are saying considering that yeah there is a equilibrium and there is a irreversible step.

But we will solve it in a different way and we are solving it under the assumption that the N_2O_2 concentration does not change over time. And we will figure out if there is an equilibrium what is the condition? Just like it there is a irreversible step; this was the condition k_2 is much much greater than k_1 .

In this case, we will see what is the condition; there is a striking difference here, here you see that it is one species going into another species, but here actually there is a bimolecular reaction going into some species. So, we there is a slight change between this steady state approximation and this steady state approximation which we are right now discussing; this steady state approximation is actually for a bimolecular reaction.

Now, let us proceed; so, what we will write is that $d N_2O_2 / dt$ that should be 0 and let us try to figure out where actually the N_2O_2 is being a formed and being consumed; now look at the first step. So, it is being formed from 2 nitric oxide molecules. So, we can write it that it is k_1 into NO square, but in the first step the reverse of the first step it is actually destroyed.

So, it is destroying at a rate of k_{-1} into N_2O_2 concentration, just the reverse step. And then again it is destroyed at a rate in the second step; so, destroying means we are writing negative sign because it is being consumed it will be $k_2 N_2O_2$ into oxygen. Now we can just arrange terms this; so, this is 0. So, you can readily figure out what is the N_2O_2 concentration; the N_2O_2 concentration will be you can see it here. So, N_2O_2 appears here N_2O_2 appears here.

So, it will be k_1 into NO concentration square divided by $k_{-1} + k_2$ into O_2 . So, the rate of the reaction which is $d N_2O_2 / dt$ with the sign that you can see that the

second step is the step whether this NO_2 is being formed. So, the rate of the reaction is the rate of the second step which is nothing, but $k_2 \text{N}_2\text{O}_2 \rightarrow \text{oxygen}$. And if we just replace the N_2O_2 concentration by the expression; what we just derived based on the steady state approximation is that; so, this is under steady state that should be 0.

So, then we get it is $k_2 k_1 \text{NO}^2$ divided by $k_{-1} + k_2 \text{O}_2$. Now you see that we have not discovered the observed rate law; we have to make a further assumption. Now what is this assumption? Now think about it once I form this N_2O_2 ; it is a it is concentration it is an intermediate and we approximated that it leads us; its concentration is steady state that is how you made it 0.

Now, the question is what are the conditions that made this steady state to be valid? Meaning if I form something the intermediate that should immediately disappear; something like for that irreversible case we said that as soon as B forms from A to B; so, then immediately it converts to C that should be that steady state; that will lead to the steady state condition which means k_2 has to be much much larger than k_{-1} .

Now, in order to understand that let us think that fine N_2O_2 is can be disappeared. So, N_2O_2 can be disappeared how N_2O_2 is formed basically in the first think about it. So, N_2O_2 is actually disappearing like this; like the reverse of this reaction. So, the reverse of the first step we can write it $k_{-1} \text{N}_2\text{O}_2$ and then there is another step which is taking it forward which is basically $k_2 \text{N}_2\text{O}_2 \rightarrow \text{oxygen}$.

Now, this is basically rate of step minus 1 minus 1 means the reverse of the step 1 and this is rate of step 2; which is step 2 which is just a forward reaction. So, the N_2O_2 is formed and then it can actually go back immediately to the reactant or actually it can immediately go to product. Now think about it if it immediately goes into the product then we will have a problem because then the product formation will be extremely fast

So, then we have an inconsistency, but we know that the product formation is not extremely fast. So, what we can do here is that we can make that as soon as N_2O_2 is formed; it actually goes back to the original state. And so, that way we can also make the N_2O_2 concentration as a steady state; instead of saying that the N_2O_2 is formed that is and it is immediately forming the product, we are saying no actually N_2O_2 is formed and immediately it goes back. Because if that the other condition is true then the product formation rate will be extremely fast.

So, that is not the situation; so we are saying that these rate of the reverse reaction of the first step is much higher than the second step and of course, the rate of formation of N_2O_2 that is also that is also much lower; I mean there is a forward step k_1 it is forming and immediately it is going; so, that is what we are saying. Now if we impose that condition you can divide both sides by N_2O_2 . So, you are saying that k_{-1} is much much greater than k_2 into O_2 .

Now, we can use this condition now into here and then we figure out that the $\frac{d[\text{O}_2]}{dt}$ will be nothing, but $k_2 k_1 [\text{NO}]^2$ divided by k_{-1} we assume that k_{-1} is much greater than k_2 into O_2 . So, now, we see that the observed rate law is the same like before there are the oxygen also we miss the oxygen here.

So, we just replaced it by N_2O_2 concentration and we wrote it like that yeah. So, we just replaced the N_2O_2 by the steady state concentration which is here and there was a k_2 times there was a oxygen. So, this is the yeah k_2 and this is the oxygen. So, we see at the end of the day this is the same rate law which we got from rate determining step approximation; however, the striking difference there are two the intermediates are different seen on case intermediate was NO_3 nitrogen trioxide and in the other case it is basically N_2O_2 .

Now, there should be some chemical or physical logic behind choosing rate determining step for one reaction involving one particular intermediate and steady state approximation for the other reaction which contain another intermediate. Now N_2O_2 nitrogen nitrous oxide it is a basically die nitrogen dioxide or something like that N_2O_2 is a very reactive spaces. So, the assumption here is that we do not see actually N_2O_2 in that in that medium.

So, then what we are saying that N_2O_2 as it is formed it immediately decomposes into a NO and 2 NO s basically ok. So, that is why the logic is something like that; now you can ask this question if you take these two steps and apply rate determining step approximation. Or if you go back and take this mechanism and apply the steady state approximation what do you get? You can actually work it out and see how you can recover that a similar rate law.

So, you work it out by yourself and see whether you are actually getting the same or similar rate law. And also you are getting the observed rate constant as a combination of

these rate constant which is k_2/k_1 by k_{-1} which are actually a rate constant for the elementary steps.

Now, to summarize we just choose only one particular reaction and we showed that how you can actually start from a you can very cleverly use these two approximation. One is a rate determining step approximation where there is a fast equilibrium followed by an slow rate determining step.

And the second one is well actually you have intermediate, but over time the intermediate concentration does not change that is known as the steady state approximation. And if you make either of these approximations then you can actually show that yes your you can actually get back your old equation older; the observed rate law which is experimentally observed. And then you can write the experimental error rate constant as a combination of all your old rate constant.

Now, remember that we gave you this example of this rate of this reaction and showed that although the rate law shows that it is a very simple straight forward thing that 2 nitric oxide molecules and 1 oxygen. And then it is giving in a square N_2O_2 , but we showed that actually the inherent mechanism of this reaction is very very different; it involves various intermediate it can it can. And it actually in this particular case to the best of my knowledge; this reaction can proceed through either of this mechanism.

So, both mechanism happen in parallel for this particular reaction and both mechanism are correct and both mechanism actually satisfactorily explain the observed rate law. So, in the following section we will start with another reaction mechanism and where we will use the steady state approximation more extensively.